

# Materials Identification and Surveillance Small Scale Reactors

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Savannah River Site

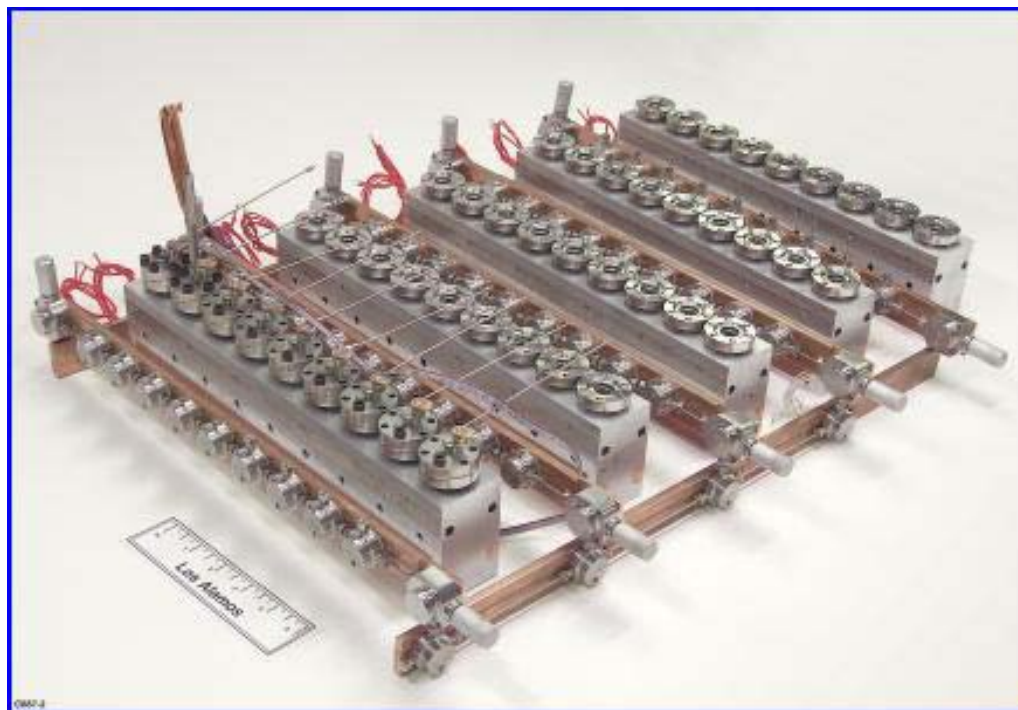
# Small Scale Reactors Outline

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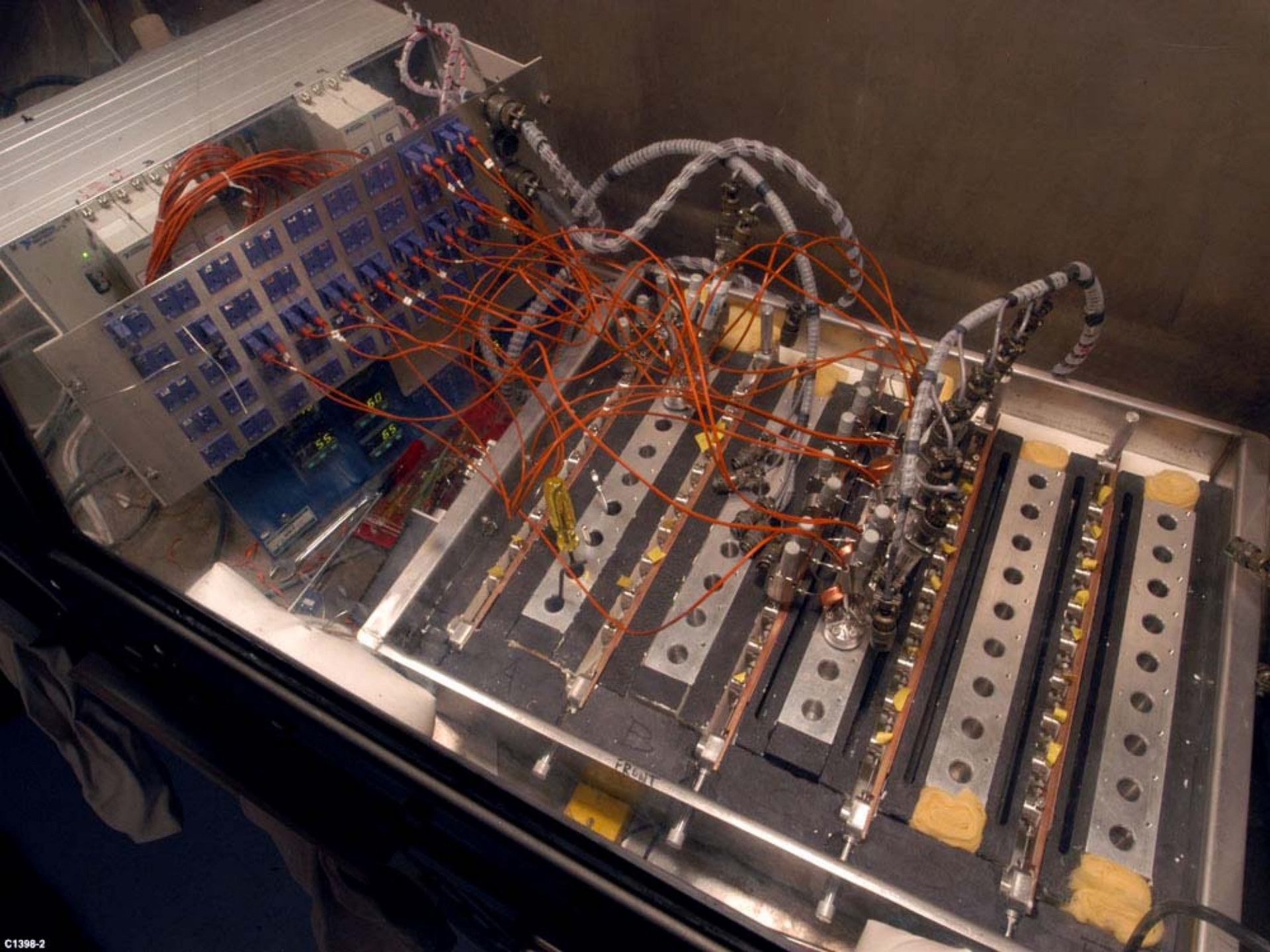
- Installation in glove box and Work Authorization
- The PF-4 Noise Problem
- Initial sample selection
- Results
- Why results are different than Duffey and Livingston
- Future work

## Small scale container surveillance samples

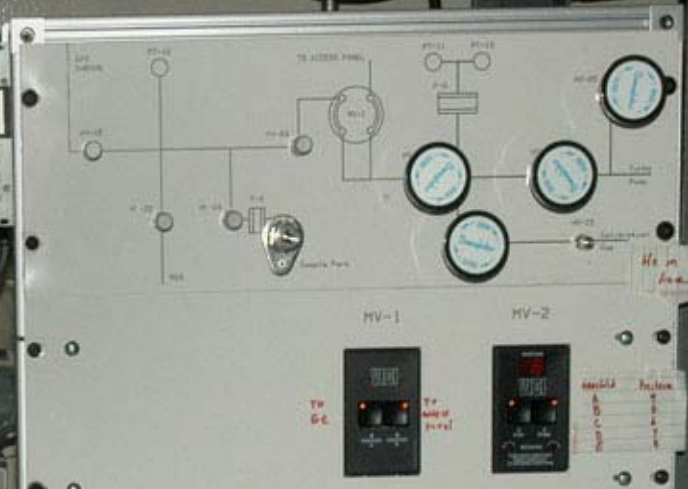
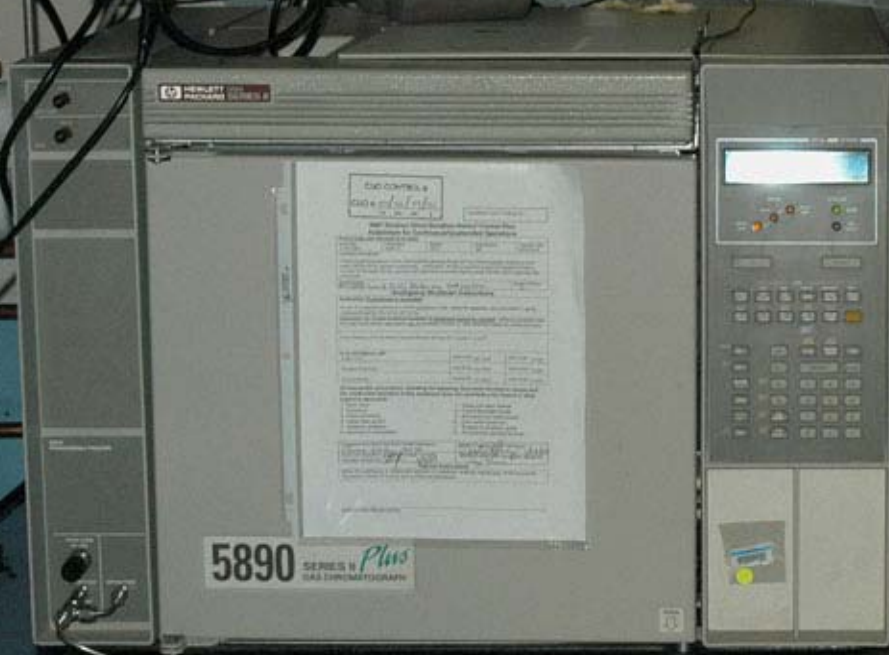
- ✧ Containers are in heated blocks (45 locations) with heated gas manifold
- ✧ Matrix assembly installed in plutonium glove box, Sept. 2002
- ✧ Plumbing complete, facility leak-tested, Dec. 2002
- ✧ First sample introduced and equipment checkout commenced, Dec. 2002
- ✧ Grandé Noise discovered, modifications tested, Jan. 2003
- ✧ Process Hazard Analysis modified, Work Instruction completed Feb. 2003
- ✧ Work and Worker Authorization and initial samples introduced Feb. 13, 2003



GC gas sampling, P/T monitoring





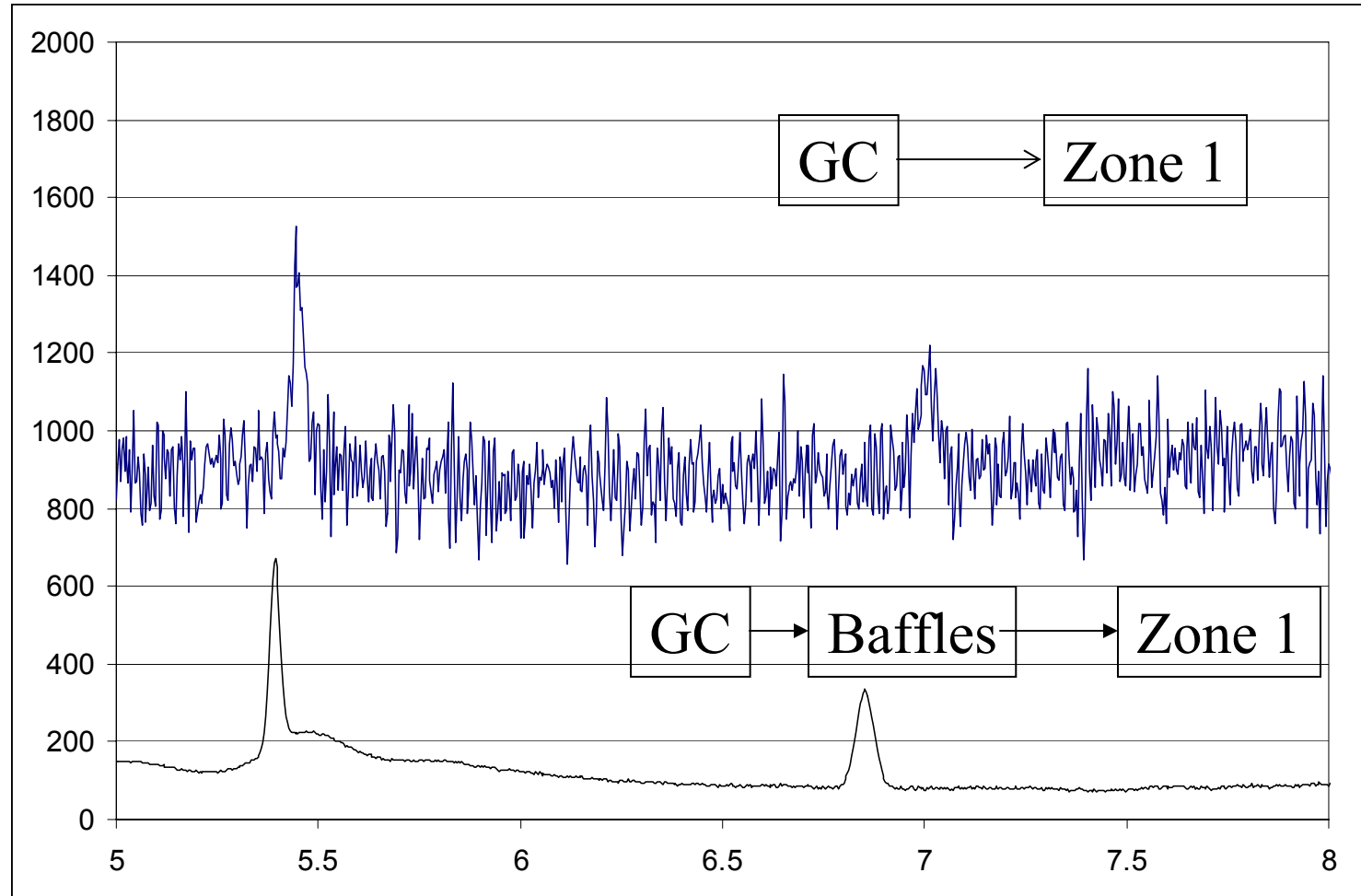






# Grandé Noise in GC spectrum

Problem diagnosed in a few days, two weeks to implement fix



JONA MACHINING COMPANY  
284 DP Road  
Las Lunas, NM 87544  
505-862-4611  
2635 Industrial Lane  
Broomfield, CO 80020  
303-438-1570

Lat. Checked  $2-1-05$   
IF: 8 am/case/11/11/05



# Initial Sample Selection Goals

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- ✧ Compare results from first Large Container material to small container configuration. Use same oxide material, keep dry, and heat to 55°C. (But did not calcine material again-material spent 12 months exposed to glove box atmosphere)
- ✧ Measure reproducibility of entire approach. Have five samples exactly the same. Chose to have these samples at 0.5 wt% water.
- ✧ Compare to Duffey and Livingston's work. One sample at 2 wt% water.

# Material Characteristics

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## PEOF1

87.81% Pu

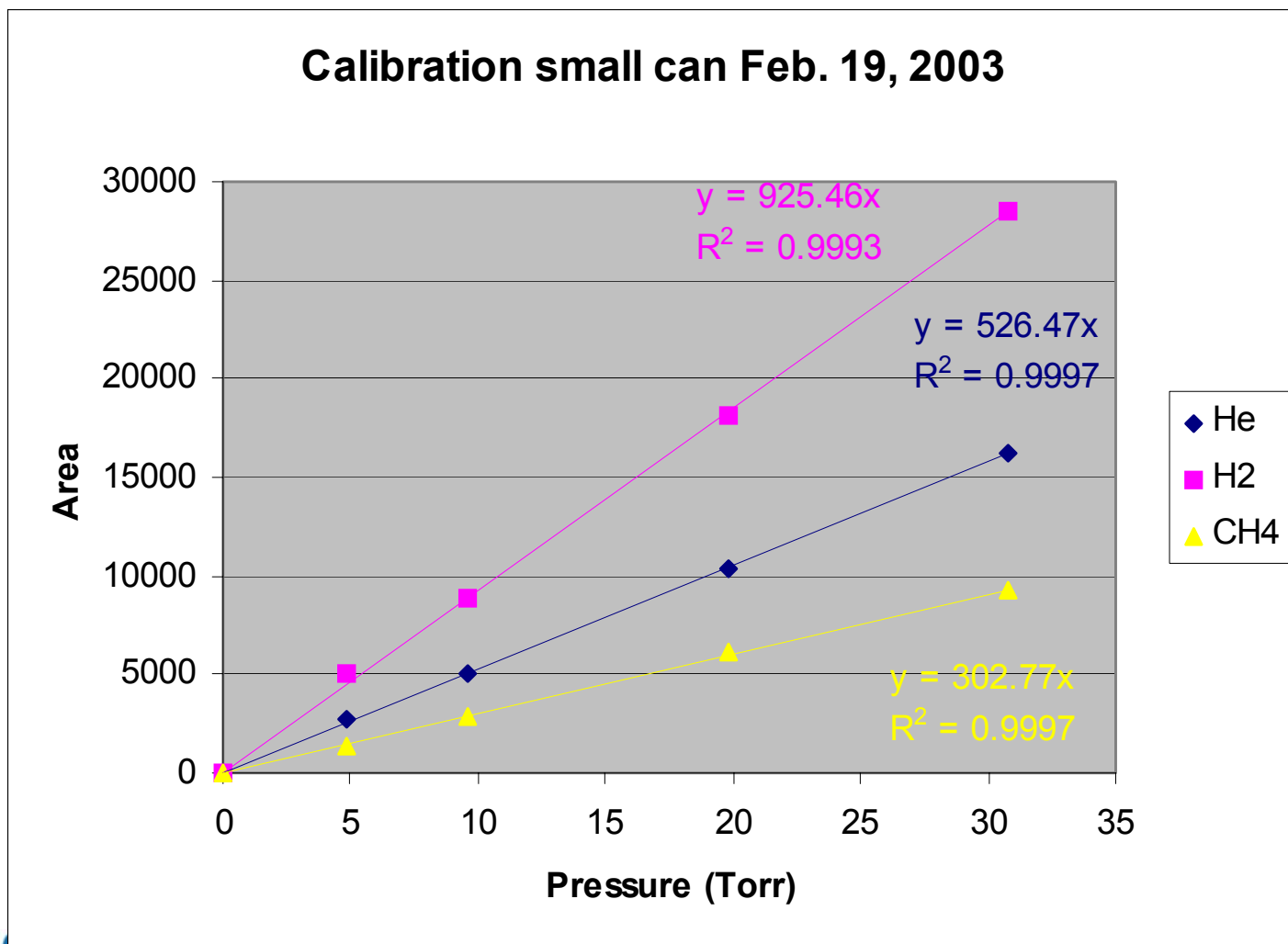
0.09% LOI (Feb 7, 2002)

1.08 m<sup>2</sup>/g SSA

11.5 g cm<sup>-3</sup> pycnometer density

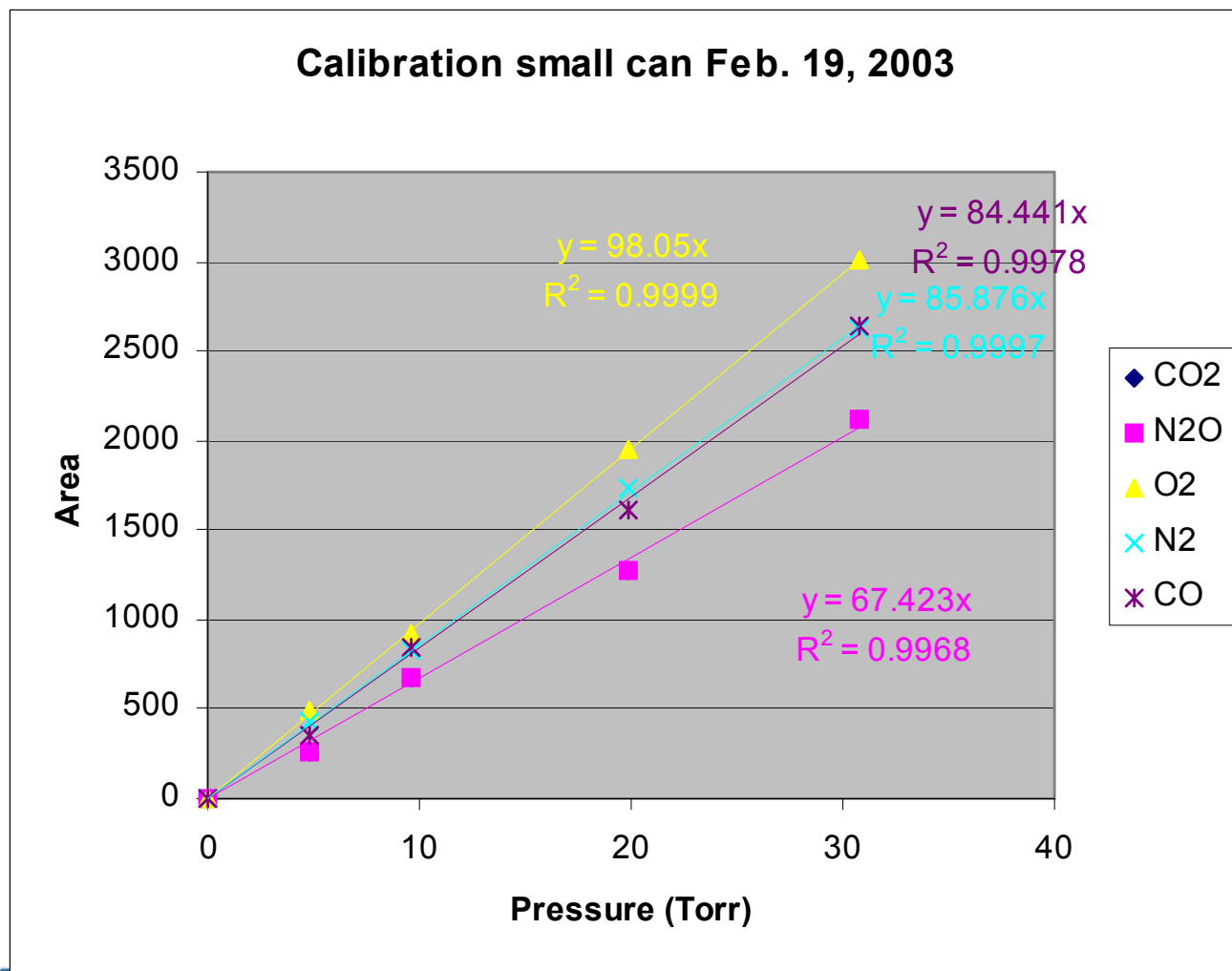
location	mass	water added	fill gas
C3	9.7 g	194 µl H <sub>2</sub> O	He
C4	10.2 g	52 µl H <sub>2</sub> O	He
C5	9.4 g	47 µl H <sub>2</sub> O	He
C6	9.1 g	45.5 µl H <sub>2</sub> O	He
C7	10.2 g	52 µl H <sub>2</sub> O	He
C8	9.3 g	47 µl H <sub>2</sub> O	He
C9	9.6 g	0 µl H <sub>2</sub> O	He

## Calibration of gases with high GC sensitivity

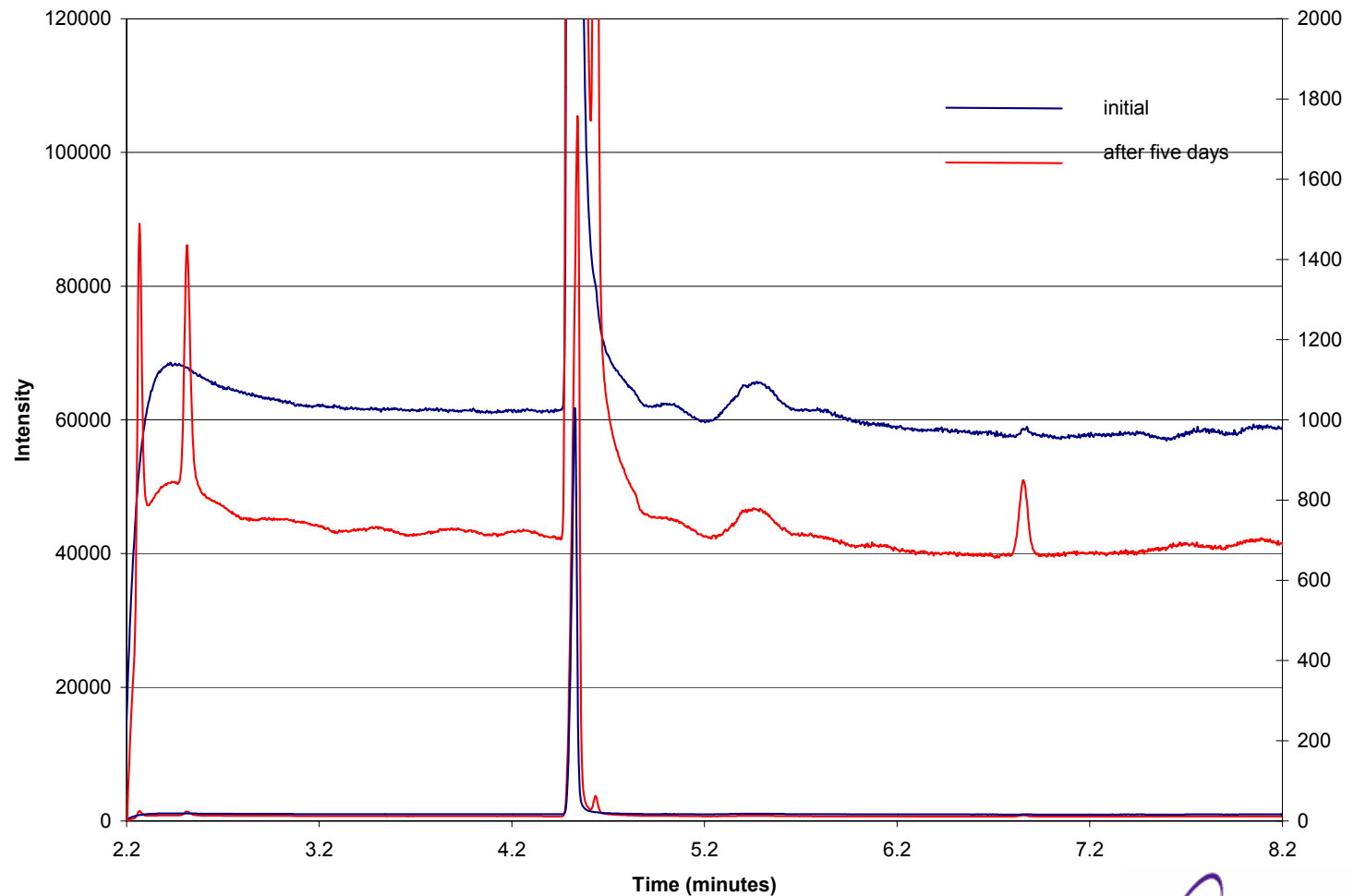




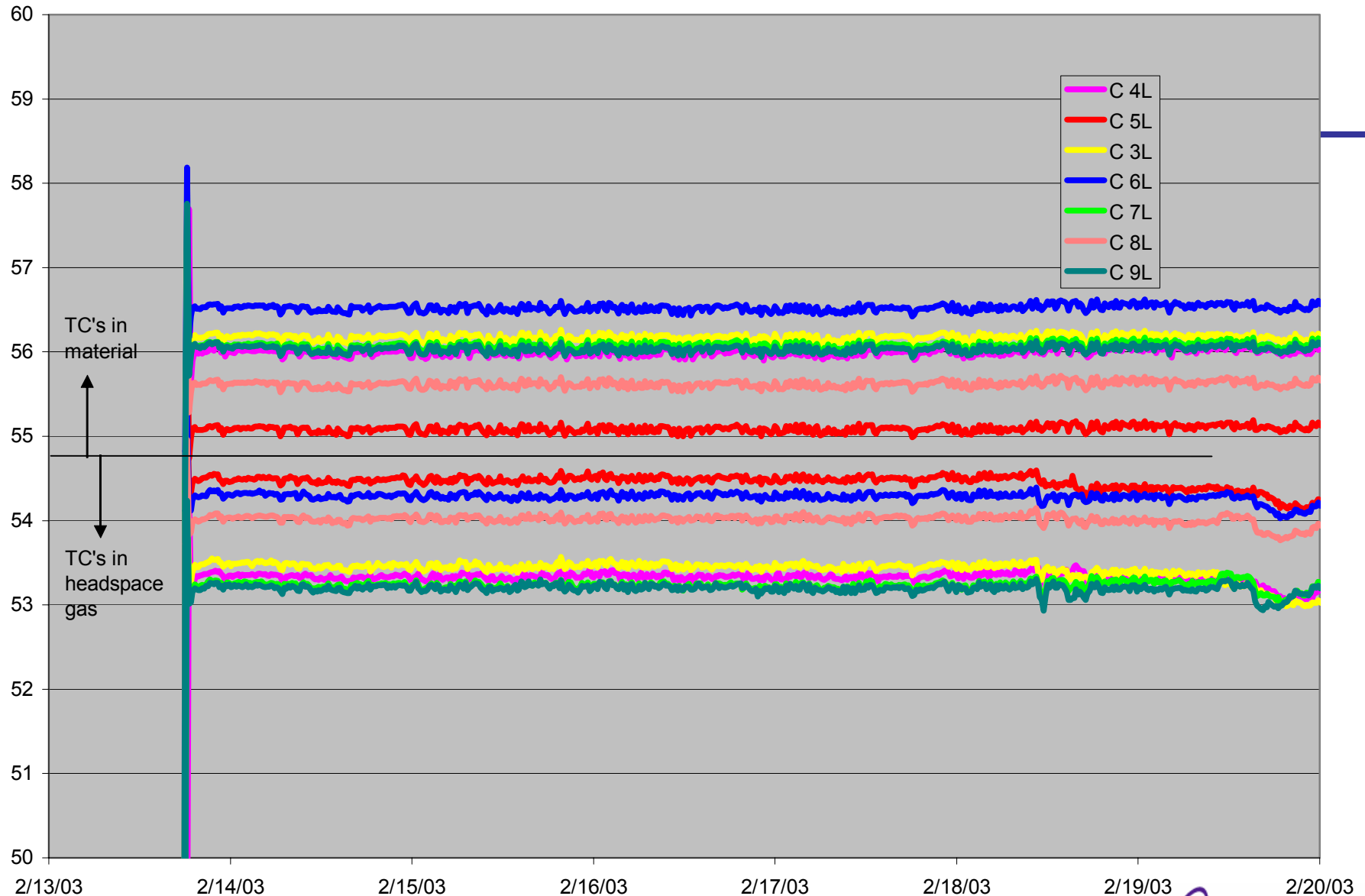
# Calibration of gases with low GC sensitivity



# GC results show significant changes in gas composition

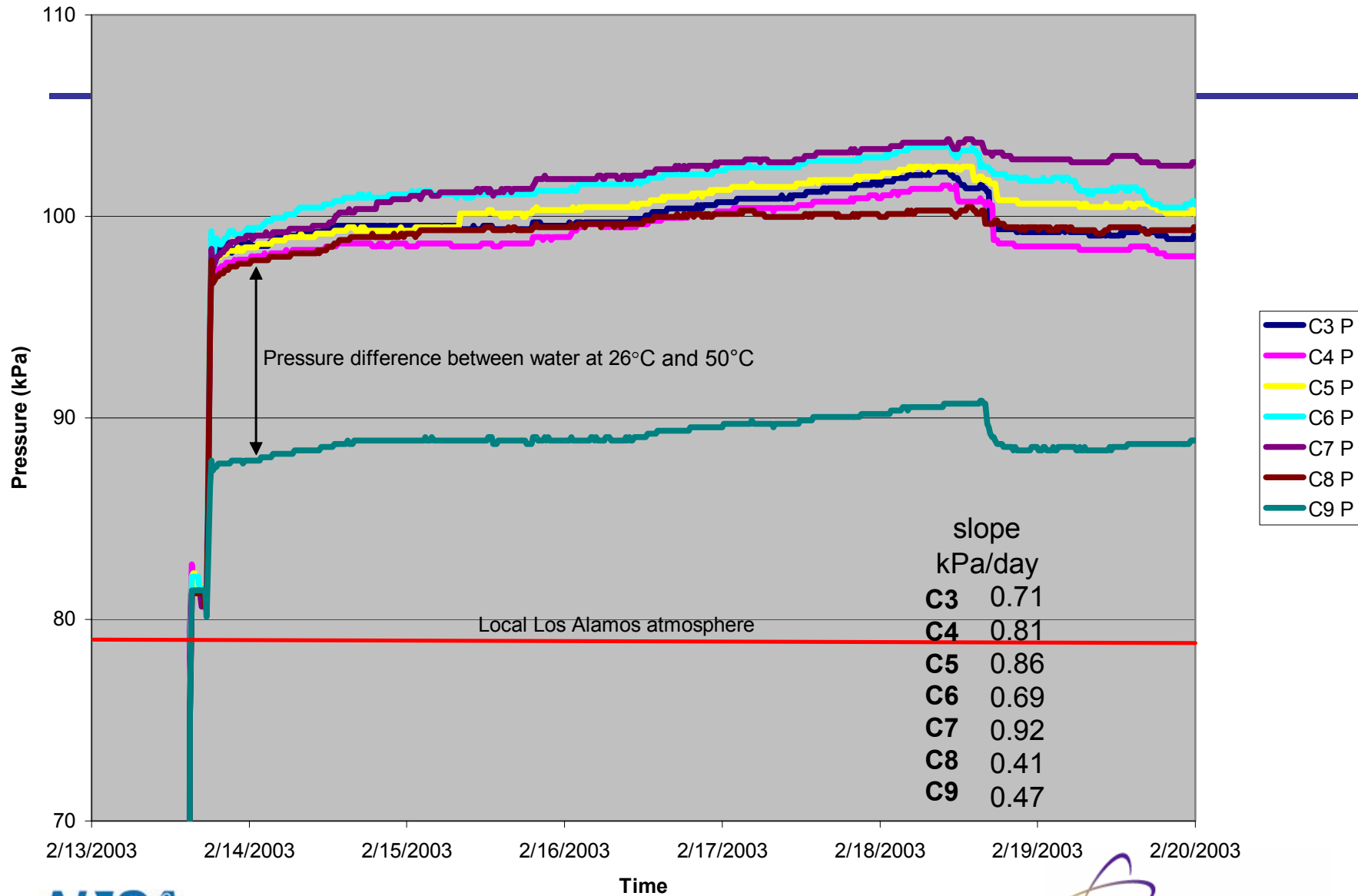


# Temperature in Small Scale Containers is Stable





# Pressure in Small Scale Containers



# Calculation Methodology

## Using Container C3 as an Example

	Integrated Area		P (Torr)		Moles in container		Change in moles	Rate of Change
	Feb. 13	Feb. 18	Feb. 13	Feb. 18	Feb. 13	Feb. 18	$10^{-6}$ moles	$\text{nmol s}^{-1} \text{ W}^{-1}$
CO <sub>2</sub>	0	1769	0.00	1.06	0	5.53E-06	5.53	0.622
N <sub>2</sub> O	0	1486	0.00	0.89	0	4.65E-06	4.65	0.522
He	259705	325074	19.75	24.72	0.000141	0.00013	-----	-----
H <sub>2</sub>	0	3467	0.00	0.15	0	7.85E-07	0.79	0.088
O <sub>2</sub>	25	25	0.01	0.01	7.27E-08	5.35E-08	-0.02	-0.002
N <sub>2</sub>	117	809	0.05	0.38	3.88E-07	1.97E-06	1.58	0.178
CO	0	200	0.00	0.10	0	4.99E-07	0.50	0.056

Sum 19.81 27.30  
Gauge 19.18 27.57

Sum of O 16.2  
Sum of N 12.5  
Sum of C 6.0

Moles of gas in one monolayer 132

## Results of Five Days Surveillance

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rate of change in nanomoles s <sup>-1</sup> W <sup>-1</sup>						
Location	CO <sub>2</sub>	N <sub>2</sub> O	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO
C3	0.622	0.522	0.088	-0.002	0.178	0.056
C4	0.619	0.647	0.098	-0.007	-0.076	0.074
C5	0.702	0.619	0.096	-0.004	0.174	0.073
C6	0.591	0.645	0.094	-0.007	0.162	0.031
C7	0.802	0.646	0.159	-0.001	0.189	0.023
C8	0.557	0.593	0.078	-0.185	-0.348	0.042
C9	0.195	0.080	0.012	0.000	0.196	0.050
Average	0.678	0.639	0.112	-0.005	0.112	0.050
Sigma	0.095	0.013	0.032	0.002	0.126	0.027



# Comparison of Initial Results to Duffey and Livingston

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H <sub>2</sub> generation rate		
	Duffey and Livingston	This Work
	nmol W <sup>-1</sup> s <sup>-1</sup>	
2 wt%	2.1 <sup>a</sup>	0.088 <sup>b</sup>
1.0 wt%	0.056 <sup>a</sup>	
0.5 wt%	0.039 <sup>b</sup>	0.112 <sup>b</sup>
0.0 wt%		0.012 <sup>b</sup>

<sup>a</sup> calcined at 700C

<sup>b</sup> calcined at 950C

Duffey and Livingston experiments at room temperature.

This work at 55C with significant temperature gradients. Liquid water likely formed on the lid, which was cooler than the material. Therefore, amount of water adsorbed onto the material is governed by the vapor pressure of water at the coolest spot, which is likely the same for 0.5wt% and 2.0wt% experiments. Thermal modeling of 3013 containers by Hensel and by Knight indicate that large temperature gradients will exist in real containers and the container walls will be the coolest areas.

## Future Work

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- Plutonium oxides of different surface areas with varying amounts of water, additional duplicates.
- Salts with varying amounts of water, duplicates.
- Laura's talk and discussion.

# Small Scale Surveillance Experimental Design

## Container Features

- 5 ml internal volume
- Scaled to 1/500th of 3013 Storage Can
- Heated to appropriate T seen in full scale containers.

## Material

- Locations contain MIS materials that meet the 3013 packaging criteria and some materials that do not meet the 3013 criteria (>0.5 wt.% moisture, calcination T)
- Initial 6 months include 5 sample blanks and 8 sample duplications
- Variables include moisture content and form of moisture (*hydrated salts, hydroxides, physisorbed water*), fill gas, temperature



## FY2002 Modifications

- ⇒ Space and safety requirements led to container lid modifications
  - More robust design for operation inside glovebox (vs. open front hood) that include new valves, pressure transducer
  - Contamination release minimized
- ⇒ GC Modifications provided increase in sample sensitivity by factor of 100.

# Small Scale P&ID Diagram

